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(54) Latent heat storage device

(57) A latent heat storage device comprises an enclosure containing a phase change material capable of prolonged supercooling. A port is provided with a penetrable soft rubber seal that may be punctured by a hollow needle which carries seed crystals. Nucleation is induced by contact between the crystals in the tip of the needle and the supercooled phase change material. The enclosure may be flexible to enable the device to be used to warm a person. Details of the enclosure needle, and materials used, are also disclosed. After discharging, the device may be recharged by way of an electrical heater inside the enclosure.

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## SPECIFICATION

## Heat retaining devices

- 5 This invention relates to phase change material and apparatus for utilising latent heat storage of such material. In particular, but not exclusively, this invention involves utilising material of the type described in published
- 10 European Patent Application 101256.
- Latent heat storage within phase change materials can be used in many ways, for both personal and object or space heating. An especially useful latent heat storage medium
- 15 such as that described in the above patent application can be supercooled for prolonged and indefinite periods while in the higher energy state, stored at ambient temperature and then triggered or nucleated when it is
- 20 desired to retrieve the stored energy. Devices incorporating this material may be recharged with energy by being heated above the transition temperature and supercooled. For use with such recyclable devices it is necessary to
- 25 provide a reliable means for repeated triggering, and preferably one that will remain reliable over the same time period as the energy storage material.
- It is also important to minimise contamination in order to produce reliable and durable
- 30 devices. Impurities may be introduced at the time of encapsulation and also along with the nucleator. In a prior art technique, a syringe is used to inject an oil carrying seed crystals into
- 35 a valve and thence into the medium to be nucleated. The problems that arise from this technique are various, for example the quantity of oil that is injected has to be sufficient to overcome a spring bias on the valve, and
- 40 after several cycles of operation this would lead to a considerable increase in the volume of material within the device. Apart from the necessity to provide an expandable container, such added material leads at best to deterioration of efficiency if the oil is inert, and
- 45 potentially to degradation of the active material. Oil also has an adverse effect upon many plastics materials and thus plastics containers may be subject to degradation. Furthermore with devices of complex geometry
- 50 (such as with interconnecting comparatively narrow passages between compartments) aggregation of the oil to form pockets could block the progression of nucleation through-
- 55 out the device.
- The present invention is directed towards providing apparatus for repeated nucleation that is consistent, and without the disadvantages of substantial volume increase.
- 60 Accordingly the present invention provides a latent heat storage device comprising an enclosure containing a phase change material in a supporting medium capable of prolonged supercooling, a closure comprising a penetrating
- 65 sealing member capable of resealing, and

a penetrating hollow needle that is adapted to induce nucleation.

- The invention is now described by way of example with reference to the accompanying drawings in which:

70 *Figures 1 to 3* show preferred embodiments of enclosures for a device according to the invention;

75 *Figures 4 to 6* are embodiments of nucleation ports and needle housings in accordance with the invention, and

*Figures 7 and 8* are respectively plan and sectional views illustrating a preferred heating method in accordance with the invention.

- 80 Some of the most useful applications of latent heat storage material are those related to the provision of personal warmth, either for medical or comfort purposes. The supercoolable latent heat storage material referred to in
- 85 the abovementioned patent application is particularly suitable for these purposes as it can be carried to remote locations and stored at ambient temperature. The present invention is described using as the preferred material a
- 90 supercoolable salt suspended in a medium comprising a microbial polysaccharide, most preferably sodium acetate trihydrate with xanthan gum, in a device suitable for providing personal warmth. Other materials that require
- 95 a similar method of nucleation or triggering could be substituted for the preferred material, and the devices on which the invention is included could be for purposes other than personal warmth and packaged in an entirely
- 100 different manner.

- Figs. 1 to 3* show flexible plastics (PVC) containers that are suitable for encapsulating sodium acetate trihydrate suspended in a xanthan gum gel for form a flexible pad. Such
- 105 flexible pads are preferred for providing personal warmth as they can be wrapped around or moulded to the contours of the body and a range of sizes of container can be provided. It is possible for the bag to be any size, but
- 110 most purposes may be suited by a bag of dimensions in the range of 8cms. square up to 1 metre square. The flexibility may be governed by several factors including shape, thickness of PVC material, interconnections or
- 115 seaming, and external structure or padding such as insulating and reflected aluminium pads which may be mounted on one side to direct heat out of the opposite side. Seaming or welding the opposite sides of the bag
- 120 together within the outer boundary may also be used as a means controlling the final thickness or cross section of the bag once filled, which in turn has an effect upon the length of time that it takes for both charging
- 125 and discharging of the device.

- The preferred method of manufacturing the pads is to fill the PVC bag through an integral filling port, preferably made as a tube extending from the bag. The filling procedure consists of warming and evacuating air from the
- 130

bag, introducing latent heat storage material (for sodium acetate suspended in xanthan gum this is preferably done at a temperature of 80°C) until the bag and filling port are full and then sealing across the filling port, for example with a radio frequency welder. The pad is then left and the material supercools to ambient temperature and remains as a soft gel. A second port in the bag is provided with a seal and an attachment (described hereinafter) for engaging a triggering apparatus. This second port is provided with its seal prior to the filling of the bag so as to ensure that there is no ingress of air or contaminants. It is possible for the ports to be concentrically arranged.

Nucleation or triggering of the device to release the stored latent heat may be achieved by mechanically introducing crystalline of sodium acetate trihydrate through the seal in the nucleation port and into contact with the supercooled gel. This commences change of the supercooled gel to the crystalline state with an accompanying release of latent heat. Once the gel has changed to the crystalline state it becomes hard and rigid, and thus so does the entire pad with a loss of flexibility. For many purposes it is desirable to retain a degree of flexibility in the pad and this is done by sectioning the bag into compartments. This may be done by providing welded lines or interconnecting several bags by thinner portions or tubes that will retain a higher degree of flexibility. If there is continuity in the latent heat storage medium then only one nucleation is necessary to discharge all the medium. In some instances it may be preferred to completely isolate the compartments and provide each with a separate nucleation port.

The patterns shown in Figs. 1 to 3 require only a single nucleation. Fig. 1 shows a simple pad and Figs. 2 and 3 show respectively pads with horizontal and vertical welds 28 and 29 which act as hinges. The basic bag comprises a pouch 21 for storing a nucleation device, a weld line 22, main body 23, nucleation port 24, natural rubber seal 25, end weld 26 and filling port 27.

Once discharged the pads may be recharged for example by submersion in a water bath at 80°C, or by electrical trace element heaters included in the bag. In this latter case a mains connection attachment can be moulded or welded integrally to the bag. With this arrangement the trace elements need to be of sufficiently low power and insulated so that the heat is dissipated at a rate that does not cause excessive local heating such as would melt the bag. Figs. 7 and 8 show an embodiment in which the heater elements are floatingly arranged for optimum surface contact. Included in the bag are a pair of coated foils 42 each with a central aperture 44 which are located in register with welded spots 43 that connect the opposite surfaces of the bag.

The foils 42 comprise a central element 46, comprising for example photodeposited or photoetched thin film elements on an insulating substrate, coated in a layer 45 of insulating material such as silicone rubber. Electrical connection is made via leads 48 which are covered in suitable plastics or rubber sheaths. The sheaths of the wires are joined in fluid tight relation to the layer 45 and via plugs 47 to the bag. Preferably the plugs are flat flange attachments to the sheath that can be welded to the bag. A socket 41 suitable for connection to mains is also provided and welded or otherwise secured to the central section of the device. With such an arrangement the foils 42 are relatively rigid and are maintained in position by the weld spots 43. The power supply is chosen so that the temperature does not exceed 80°C. Recharging time depends upon the relative size of the element surface and the depth of material latent heat storage material covering the surface, but in general it will take several hours with 3 to 8 hours being the preferred range for convenient use.

Referring now to Figs. 4 to 6, the nucleation port 24 comprises a rigid tube 1 which may be made integrally with the PVC bag and which serves as a guide for a nucleation device shown generally as 32. The nucleation devices operate on the principle of injecting a hypodermic needle through a rubber seal into the latent heat storage material. The hollow of the needle is charged with sodium acetate (or other nucleator) crystals. Once the needle is withdrawn the rubber seal reseals. The needle may be charged in the first instance by dipping the needle into molten sodium acetate trihydrate which is sucked up and subsequently crystallised. Although the quantity of material within the needle is very small (the needle having an external diameter of about 0.5 mm) nucleation is achieved by such a small quantity of material that deposition of or contact with the outermost crystal of the needle bore is sufficient and the needle can contain sufficient crystals for about 30 nucleation operations.

In Figs. 4 and 5 the nucleation port 1 is sealed by a soft grade natural rubber seal 25 which is retained in position by PVC tubular portions 3 and 4 which constitute a seal keep and needle guide respectively. The nucleation device can be disengaged from the port 24, and comprises a fine hypodermic needle 5 charged with crystals, a needle housing 6 and body 7, a spring 8 for retracting the needle and a plunger 9. In the embodiment shown in Fig. 5 the plunger comprises a press top that slides over the body, a spring locating member 10 and a shaft locating screw 11. In this embodiment the spring is locked until the plunger cap is rotated 45° and the locating member engaged, thus the device can be mounted ready for triggering with a safety mechanism to prevent accidental triggering.

For general storage and when the pad is being heated for reuse the nucleation devices can be removed, and in this instance the locking mechanism of Fig. 5 prevents possible injury. A cap may be provided for insertion over the nucleation port as an additional precaution against ingress or egress of substances. It will be noted that an insignificant quantity of material is added to the container, and nucleation of sodium acetate with sodium acetate trihydrate crystals enables the added material to be incorporated as part of the active medium in future cycles of operation.

In normal use crystals provided in the needle as described above are satisfactory, however it is possible for the crystals to deteriorate, due for example to moisture loss in prolonged periods of storage, and also in due course the supply becomes exhausted even though the remainder of the apparatus may still be capable of operation. In order to ensure that the nucleation device is functional at the time of sale, and also to provide a means for recharging the needle, sodium acetate trihydrate crystals are combined with a moisture retaining suspending medium.

A suitable suspension may be formed by combining a wax that melts at about 49°C, with a thickening agent that will thicken non-polar solutions, for example that sold under the trade name Cab-o-sil. The wax is heated above its melting temperature to about 60°C or 65°C, and Cab-o-sil equal to about 8% by weight of the wax is added and the mixture is maintained at 60°C. About 1.5 times the weight of the wax of sodium acetate trihydrate crystals (or other nucleating agent) are finely crushed and added to the mixture and quickly mixed in to form a slurry which is then poured into a mixture is slightly above the melting temperature of sodium acetate trihydrate there in insufficient heat to melt the large quantity of powdered crystal that is added.

The tip of a hollow needle may be charged with the wax and crystal suspension by plunging the needle into the solidified mixture. The solid wax acts to ensure that the crystals within the wax retain their moisture, without preventing the crystals from inducing nucleation when the crystal and wax mixture is introduced to the supercooled gel, and further prevent any crystals further within the needle from drying out. The keeping properties of the wax mixture enable small containers of the wax to be provided for periodic recharging of the needle of the nucleating device should this become necessary such as after prolonged periods between use. The use of the wax suspension does involve the addition of an inactive contaminant to the latent heat storage material. However as the nucleator is passively added, that is a significant volume of material is not forcibly ejected to admix, the quantity of contaminant added is exceedingly small. Indeed it is possible to regard the

end surface of the wax as a reusable nucleation surface.

In the embodiment shown in Fig. 6 the needle of the nucleator assembly is adapted to be retained in position in contact with the latent heat storage material once it has been used to trigger energy release. Thus the hollow needle 5 becomes surrounded by the crystalline material as it changes phase, and crystals become engaged in any available space in the bore to 'recharge' the needle. The needle assembly is withdrawn before the bag is heated to change the storage medium back to the higher energy state. It will be noted that with this embodiment there is no net addition of material: as crystal is eroded from the end of the needle it is replaced by other crystal and withdrawn. A removable cap 30 for the needle assembly is provided with a suspended wax and crystal plug 31 covered by a seal 33 into which the needle can be plunged for storage. This plug prevents the crystals in the needle from drying out and also provide a reliable source for recharging the needle in the event of failure of in situ charging.

In a preferred method of manufacturing a heat retaining device in accordance with the invention the nucleation port is utilised in the filling process and the needle is simultaneously charged with gel which subsequently crystallises. This is achieved by inserting at least the needle of the needle assembly through the seal of the nucleation port and attaching the outward end of the needle to the pump for evacuating the bag. The latent heat storage material is then introduced through the filling port and into the bag. If the bag is evacuated through the filling port and then filled a residual pocket of air tends to be retained, usually up against the nucleation seal. However, by evacuating the bag via the needle it is possible to eliminate this air pocket and fill the bag right up to the seal. Using this technique the material is also introduced into the needle itself. The filling port is then sealed, the needle removed and disconnected from the pump and the housing for the needle assembly completed. An end cap containing a suspended wax and crystal plug is then placed over the needle and contact with the wax causes the gel in the needle to crystallise. When the end cap is removed for first use the needle is charged with crystals that have been protected by the plug, and also the end of the needle is charged with the wax suspension. The presence of the crystals in the needle ensures in-situ recharging and the repeated nucleation is minimum contamination to the material within the bag. An alternative cap or a two section cap may be provided for storing the needle without replacement in the wax, with the wax plug remaining available for use when necessary such as after long periods of storage.

## CLAIMS

1. A latent heat storage device comprising an enclosure containing a phase change material in a supporting medium capable of prolonged supercooling, a closure comprising a penetrable sealing member capable of re-sealing, and a penetrating hollow needle that is adapted to induce nucleation.
2. A latent heat storage device according to claim 1 wherein the seal comprises soft rubber.
3. A latent heat storage device according to claim 1 or claim 2 in which the needle contains solid nucleation inducing substance.
4. A latent heat storage device comprising an enclosure containing a phase change material capable of prolonged supercooling, a nucleation port comprising a penetrable sealing member capable of resealing after being penetrated and a hollow needle in a housing, the needle being positioned within the housing for direction at the seal upon engagement between the housing and the nucleation port and containing a nucleation inducing substance.
5. A device according to claim 4 in which the end of the needle contains a nucleation inducing substance in a solidified matrix comprising wax and a thickening agent.
6. A device according to claim 4 in which the needle housing is adapted to position the needle in contact with the phase change material and maintain contact at least until nucleation has proceeded in the vicinity of the needle.
7. A device according to claim 6 in which the needle withdraws crystalline phase change material from the enclosure as it is withdrawn through the seal.
8. A device according to any preceding claim in which the hollow needle contains crystals of phase change material.
9. A device according to any preceding claim in which the enclosure comprises a flexible plastics container divided into a plurality of compartments by at least one partition line, the phase change material with in each compartment being contiguous and the device being capable of flexure along the partition line.
10. Apparatus according to any preceding claim further comprising a removeable cap for the needle, the cap having an insert of a wax, suspending agent and crystalline nucleating substance into which the needle can be plunged.
11. A method of manufacturing a latent heat storage device comprising providing a container having an inlet opening and an outlet opening with a closable seal, inserting a member through the seal to provide communication from the interior of the container to the exterior, evacuating air from the container via the outlet and introducing latent heat storage

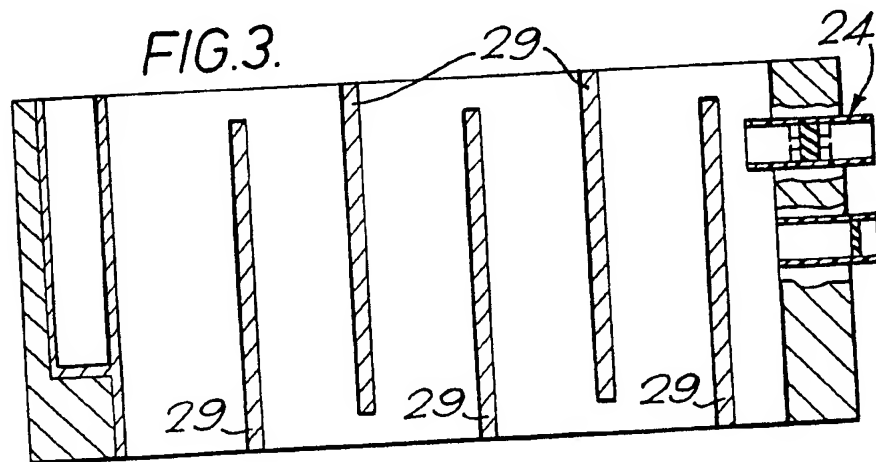
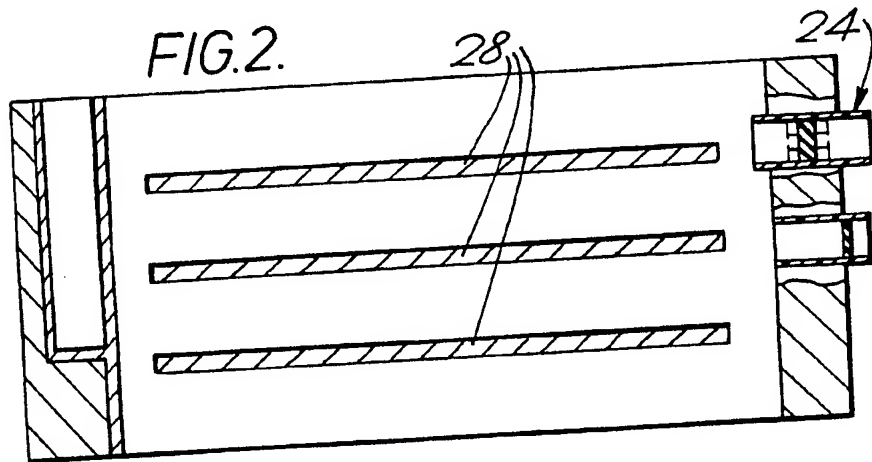
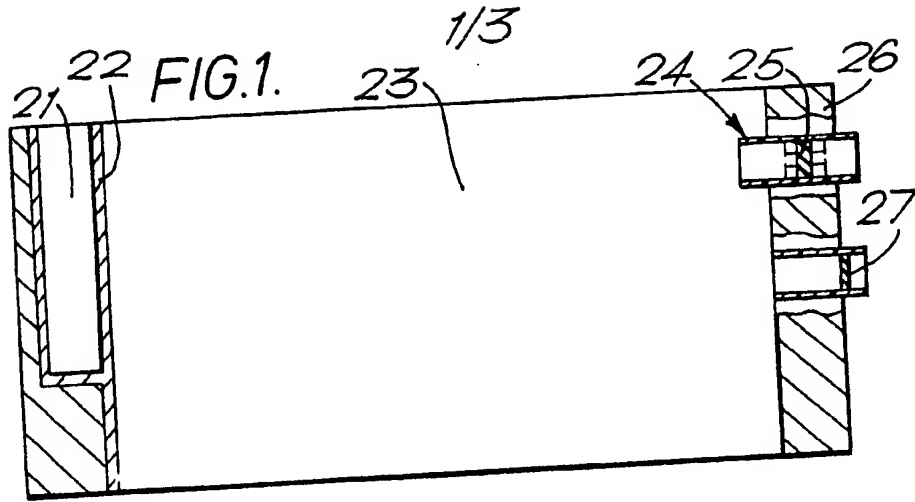
material via the inlet into the container and member, closing the inlet, withdrawing the member leaving the outlet sealed, and recrystallising the material in the member to form a nucleator that upon reintroduction of the member through the seal nucleates recrystallisation of the material in the container.

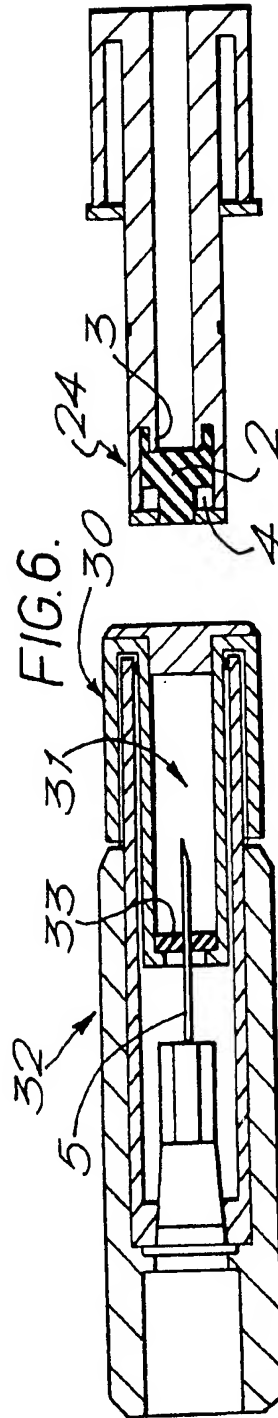
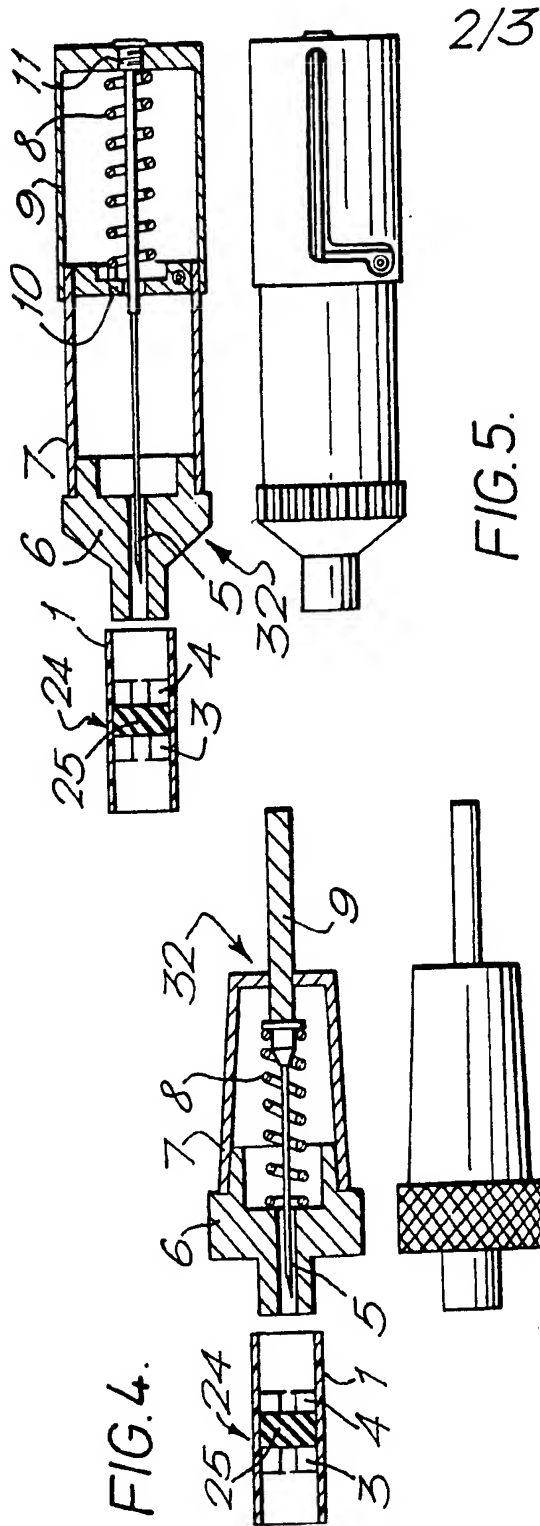
12. A latent heat storage device comprising an enclosure containing a phase change material in a supporting medium capable of prolonged supercooling and an electrical heating element included in the enclosure.

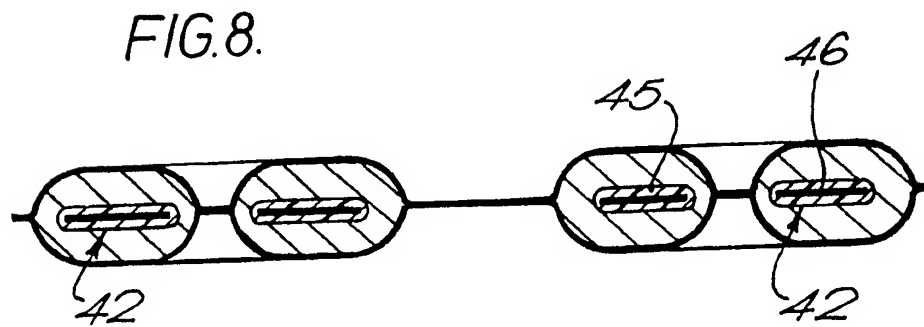
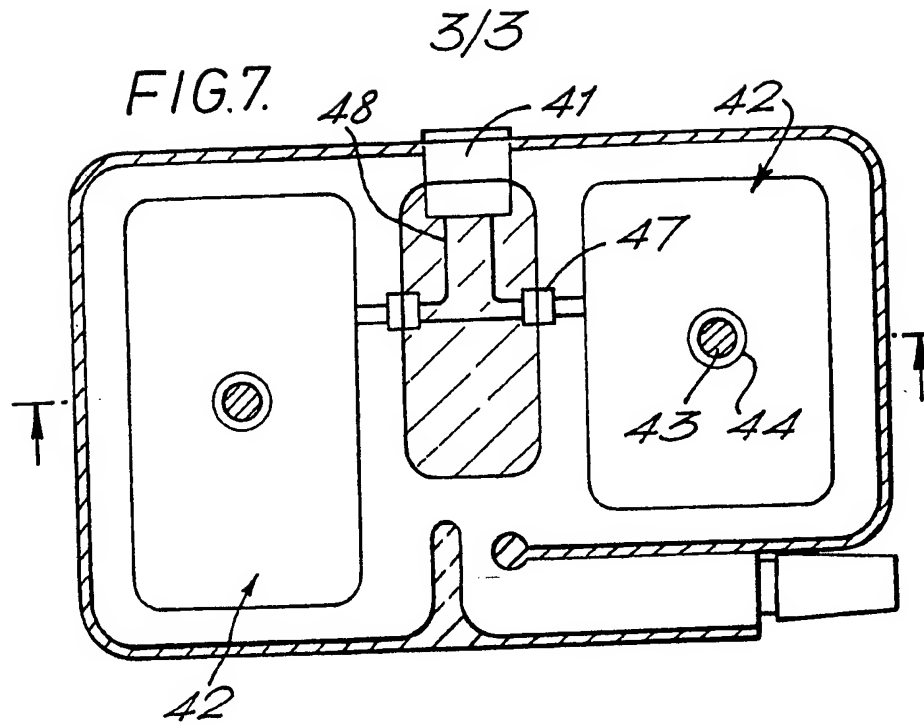
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TITLE: Latent heat storage device - has flexible enclosure contg. phase change material activated by hollow needle carrying seed crystals

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BASIC-ABSTRACT: The latent heat storage device comprises an enclosure containing a phase change material capable of prolonged supercooling. A port is provided with a penetrable soft rubber seal that may be punctured by a hollow needle which carries seed crystals. Nucleation is induced by contact between the crystals in the tip of the needle and the supercooled phase change material.

The enclosure may be flexible to enable the device to be used to warm a person. After discharging, the device may be recharged by an electrical heater inside the enclosure.

